

# Degradation of refractory compounds in industrial wastewaters by advanced technologies based on electrochemical and photochemical oxidation

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**Abstract** Results are presented of a systematic experimental investigation aiming to eliminate refractory organics from industrial effluents, of high and non-biodegradable organic load, by two Advanced Oxidation Processes (AOPs). Bench scale experiments were performed with real wastewater samples collected from a pesticides manufacturing plant, of varying TOC content (800-1820 mg/L), to investigate the effectiveness of boron-doped diamond (BDD) anodic oxidation (AO), of H<sub>2</sub>O<sub>2</sub> photolysis with UV-C irradiation (H<sub>2</sub>O<sub>2</sub>/UV-C), and their combination (i.e. AO/H<sub>2</sub>O<sub>2</sub>/UV-C) on the total organic carbon (TOC) removal. The effect of main operating conditions was investigated for both processes, separately and in combination. In the case of AO, TOC and COD were removed at a rate of 36.4 mgC/h and 89.5 mgO<sub>2</sub>/L, by applying a current density of 100 mA/cm<sup>2</sup> and a recirculation flow rate of 1400 mL/min. The H<sub>2</sub>O<sub>2</sub>/UV-C process achieved a TOC removal rate of 369 mgC/h and over 98% color removal after 4 h of treatment, when a single dose of 6 g/L H<sub>2</sub>O<sub>2</sub> and 11.8 W/L of UVC irradiation dose were applied. Finally, the combined process (AO/H<sub>2</sub>O<sub>2</sub>/UV-C) led to a faster TOC abatement (534 mgC/h) and a higher color removal, after treating the wastewater with 77 mA/cm<sup>2</sup> current density, 5.9 W/L UVC irradiation dose and ‘on-line’ dosing 15.7 g/L H<sub>2</sub>O<sub>2</sub>.

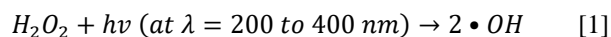
**Keywords:** wastewater, refractory organics, electrochemical advanced oxidation processes, anodic oxidation, photochemical oxidation, pesticides industry

## 1. Introduction

One of the major challenges that chemical industries face today is the efficient treatment of wastewater with environmentally and economically viable technologies that meet stringent legal limits for safe disposal and/or reuse in the production process. The challenge is particularly critical considering that most of these effluents contain toxic and non-biodegradable organic materials (paints, solvents, pesticides, pharmaceutical

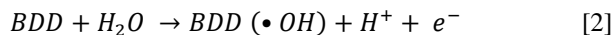
substances, detergents, hydrocarbons, etc.) whose degradation/mineralization requires adoption of costly processing methods. The latter face environmental issues (e.g., safe disposal of depleted sorbent materials with high toxicity, membrane process concentrate, etc.), in addition to their inherent problems; e.g. saturation and frequent regeneration of sorbent materials, such as activated carbon, transport, storage and /or production of oxidizing agents such as H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, etc. Advanced Oxidation Processes (AOPs) are considered promising alternatives to conventional methods for the efficient and cost-effective removal of refractory organic pollutants from water and wastewater (Brillas and Martínez-Huitle, 2015; Oturan and Aaron, 2014). AOPs are based on the in-situ production of hydroxyl radical (•OH) which is the second strongest oxidizing agent after fluorine. It destroys most organic and organometallic pollutants until total mineralization, i.e., conversion to CO<sub>2</sub>, water, and inorganic ions. Because of its activity, •OH tends to be short-lived in the solution and non-selective in its attack on electron-rich bonds.

A well-known AOP with commercial applications is the photolytic decomposition of H<sub>2</sub>O<sub>2</sub> with UV-C irradiation (H<sub>2</sub>O<sub>2</sub>/UV-C process), which results in the formation of strong oxidizing compounds (i.e., hydroxyl radicals) according to the following reaction (cleavage of the O-O bond):



In parallel, the convenient application of electrical current, instead of chemicals, prompted researchers to develop electrochemical wastewater treatment technologies for the prevention of pollution problems (Brillas et al., 2009). Electro-Fenton (EF) and Anodic oxidation (AO) are major representatives of the electrochemical advanced oxidation processes (EAOPs) that have been proven very effective towards the degradation and mineralization of recalcitrant organics. In AO, •OH are heterogeneously electrogenerated at the surface of a high O<sub>2</sub>-overvoltage anode from water oxidation. According to literature, Boron-doped

Diamond (BDD) is the optimal electrode material as it has good physical and chemical properties (Panizza and Cerisola, 2005; He et al., 2019) and presents very high O<sub>2</sub> overpotential that enhance the production of •OH and minimize the O<sub>2</sub> evolution reaction:



In the present study, the AO and the H<sub>2</sub>O<sub>2</sub>/UV-C processes, alone or in combination, were successfully tested for the elimination of toxic and non-biodegradable organic materials from wastewater of a Greek pesticides manufacturing plant, thus paving the way for process optimization and industrial application.

## 2. Materials and Methods

### 2.1. Materials and chemical reagents

The wastewater used for the experiments was supplied by K&N Efthymiadis S.A, a company which specializes in the development, production and distribution of plant protection products and specialized fertilizers. The range of the physicochemical properties of the wastewater used was as follows: pH 5.3-6.1, eC 1772-2150 µS/cm, TOC 800-1820 mg/L, TN 120-1415 mg/L, COD 1398-7400 mg/L, TP 231-500 mg/L. The electrochemical cell employed was equipped with a carbon-polytetrafluoroethylene (PTFE) as the cathode (Gaskatel GmbH, Germany), reinforced with a Nickel (Ni) mesh (GDE-Ni), and a Boron Doped Diamond (BDD) electrode as the anode (Electro Cell S/A, Denmark). Four low pressure mercury-vapor lamps (TUV PL-L 24W Philips), emitting at 253.7 nm were employed as UV-C light source to the system. Sodium sulfate anhydrous (Na<sub>2</sub>SO<sub>4</sub>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) solution 30% w/w were supplied by Chem-Lab. The H<sub>2</sub>O<sub>2</sub> solutions were prepared with deionized water (DI) produced from groundwater by a reverse osmosis system.

### 2.2 Analytical methods

Total Organic Carbon (TOC) and Total Nitrogen (TN) concentrations were measured directly by employing a TOC/TN analyzer. The Chemical Oxygen Demand (COD) and the Total Phosphate (TP) determination were made colorimetrically according to APHA 5220 D and APHA 4500-P methods, respectively. For the color measurements, the samples were first treated with 0.45 µm filters of Nylon fiber. For the colorimetric methods and UV<sub>254</sub> absorbance a photospectrometer device was used. The pH and electrical conductivity (eC) were determined with a bench scale digital polyme-ter. Finally, light intensity of lamps was measured with a portable radiometer equipped with a UV-C sensor.

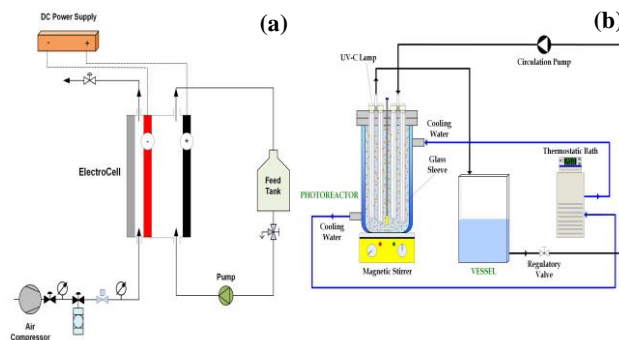
### 2.3 Experimental set-ups and procedures

The bench-scale electrochemical oxidation (EO) set-up (Fig. 1a) used in this study comprises a plate-and-frame electrochemical cell (Micro Flow Cell by ElectroCell, Denmark), a 1 L feed water tank, a recirculation pump and a power supply. Sensors are located at inlet and outlet of the cell, measuring operating variables, such as

flow rate, pH, temperature, oxidation-reduction potential (ORP) and pressure. The experimental set-up is equipped with a Supervisory Control and Data Acquisition (SCADA) system for recording the aforementioned operating parameters and for overall monitoring/control through a PLC unit, a touch screen Human Machine Interface (HMI), and other expansion electronic modules. Batch experiments under galvanostatic conditions, were conducted regarding anodic oxidation. The total test duration was varied between 2 to 24h and the total treated volume was 500 mL. First, the wastewater was treated with a 1.5 µm glass fiber filter, in order to remove the suspended particles and to prevent deposition on the electrode surfaces. Afterwards, this fluid was introduced to the vessel and recirculation began between the vessel and the electrochemical cell for 5 min without applying current. Finally, constant current was applied to the system through the power supply until the end of the experiment.

The experimental photochemical oxidation (H<sub>2</sub>O<sub>2</sub>/UV-C) set-up (Fig. 1b) consisted mainly of a photoreactor and a vessel. The photoreactor was a double-wall cylindrical vessel made of stainless steel. Four quartz close-ended glass sleeves were immersed vertically inside the reactor with the encased lamps. A rectangular Plexiglas® vessel was employed to enlarge the total working volume (4L) and to provide a clear optical view of the treated solution. A thermostatic bath was used to control the reaction temperature at the desirable constant level. In the tests, the wastewater was first added to the photoreactor. Next, it was recirculated between the photoreactor and the Plexiglas® vessel, in the dark (without UV-C irradiation), for about 10 min, to achieve homogeneity. Finally, lamps were switched on, denoting time zero (t=0), and the experiment was started. At the same time the batch addition of H<sub>2</sub>O<sub>2</sub> solution into the reactor was made. All the experiments were carried out for 4h.

In the mode involving combined AO and H<sub>2</sub>O<sub>2</sub>/UV-C treatment, the wastewater outlet from the electrochemical cell was driven directly into the photoreactor and then recirculated between the photoreactor and the cell. A dosing pump was responsible for the ‘on-line’ addition of a known concentration of H<sub>2</sub>O<sub>2</sub> solution with constant rate, in an effort to simulate real industrial conditions. Total treated volume was 5L and the total treatment time 6 or 12h.



**Figure 1.** Experimental set-up of (a) AO and (b) H<sub>2</sub>O<sub>2</sub>/UV-C processes.

### 3. Experimental Results

#### 3.1 Electrochemical Oxidation

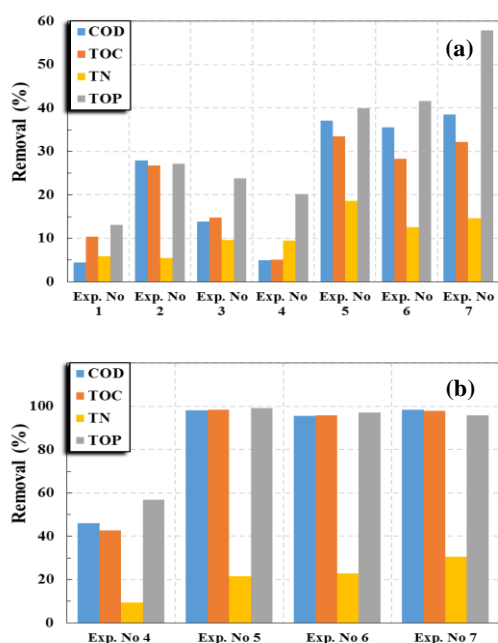
Seven experiments were carried out in order to examine the system performance at different operating conditions (Table 1). The effectiveness of the system was evaluated for 2h electrolysis time in all experiments (Fig. 2a), whereas the duration was extended to 24h for Exp. No 4 and 5, and to 12h for Exp. No 6 and 7 (Fig. 2b).

**Table 1.** Main experimental conditions of electrochemical oxidation.

Exp. No	Na <sub>2</sub> SO <sub>4</sub> (mM)	eC (μS/cm)	Air Flow (L/min)	Flow (mL/min)	CD (mA/cm <sup>2</sup> )
1	0	2020	0	60	20
2	50	11700	0	60	150
3	0	2010	1.8	60	20
4	0	2140	0	60	20
5	0	1986	0	1000	65
6	0	2050	0	1400	100
7	0	2010	1.8	1400	100

eC:electrical Conductivity, CD:Current Density

From Exp. No 1 and 2 results (Fig. 2a) it is observed that the addition of electrolyte improves the system efficiency, due to the higher current densities applied (removal of COD from ~ 5% to ~28% and TOC from ~10.5% to ~27%). At similar current density (20 mA/cm<sup>2</sup>) the supply of air improved the removal of COD and TOC (Exp. No 3) probably due to the synergistic action of other oxidants formed in the bulk (H<sub>2</sub>O<sub>2</sub> and •OH by the electro-Fenton reaction due the presence of Fe species in the wastewater). At 20 mA/cm<sup>2</sup>, low feed flow rate (60 mL/min) and no supply of air, the longer electrolysis time (extended to 24h) did not lead to improved organics abatement (Exp. No 4). This means that at the specified conditions no further oxidation of the formed organic by-products is possible.



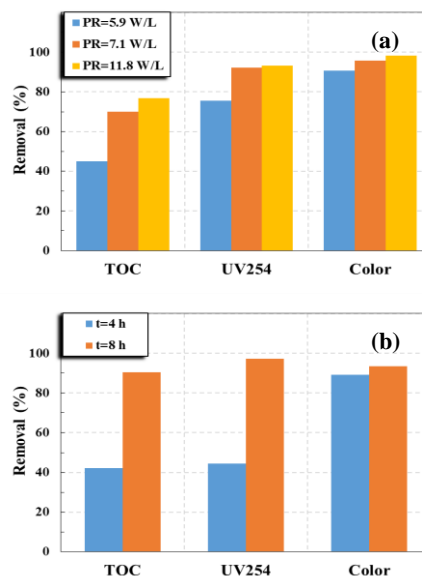
**Figure 2.** Performance of BDD anodic oxidation after (a) 2h (Exp. No 1-7), (b) 24h (Exp. No 4-5) and 12h (Exp. No 6-7)

According to Fig. 2b, the increase of the feed flow rate from 60 to 1000 mL/min had a positive effect on the elimination of the organics, since both COD and TOC removals were higher than 40% after 2h of treatment and approx. 100% after 24h (Exp. No 5). Although the residence time of the treated wastewater decreases with the flow, the improved turbidity in the cell (promoted by the spacer placed between the two electrodes) seems to enhance the mass transfer of the organics to the anode electrode surface, and therefore the reaction with the short-lived BDD(•OH) (half time of a few nanoseconds). Moreover, the higher flow rate favors the removal of gases produced by the mineralization of the organics during the electrolysis, thus lowering the ohmic resistance in the cell and increasing the applied current density from 20 to 65 mA/cm<sup>2</sup>. The same stands for Exp. No 6, since an increase of the flow rate to 1400 mL/min resulted in an increased CD to 100 mA/cm<sup>2</sup> which in turn led to an almost complete COD and TOC removal at half of the time compared to Exp. No 5. Finally, the supply of air to the GDE cathode (Exp. No 7) did not alter significantly the overall performance.

#### 3.2 Photochemical Oxidation

The main experimental results of the H<sub>2</sub>O<sub>2</sub>/UV-C process are presented in Fig. 3. The addition of H<sub>2</sub>O<sub>2</sub> in photochemical oxidation experiments was characterized as “batch” addition, meaning that the entire appropriate volume of H<sub>2</sub>O<sub>2</sub> was added inside the photoreactor at the beginning of the experiment.

Radiant power per unit volume (P<sub>R</sub>) seems to have a significant positive effect on the overall system efficiency, as expected. Specifically, doubling the P<sub>R</sub> value from 5.9 to 11.8 W/L (4 instead of 2 lamps used) led to an increase of approx. 70% and 23% concerning TOC and UV<sub>254</sub> removal respectively, when 6 g/L H<sub>2</sub>O<sub>2</sub> were added (Fig 3a).

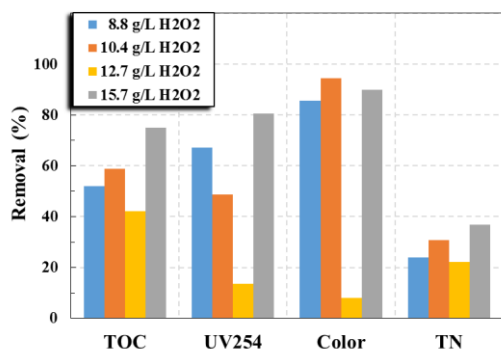


**Figure 3.** Effect of (a) radiant power per unit volume and (b) operation time on photochemical oxidation performance after treatment with H<sub>2</sub>O<sub>2</sub>/UV-C. (a) 6 g/L H<sub>2</sub>O<sub>2</sub>, 4h (b) 3.38 W/L, 12 g/L H<sub>2</sub>O<sub>2</sub>

In addition, almost complete discoloration (>90%) of wastewater was achieved after 4h treatment in all tests. Furthermore, the process operating time extension from 4h to 8h, also had a great positive effect on percentage removal of main parameters, as shown in Fig. 3b. TOC removal increased up to 48 percentage units; i.e., from 42 to 90% and UV<sub>254</sub> up to 53 percentage units; i.e., from 44 to 97% respectively, when 12 g/L H<sub>2</sub>O<sub>2</sub> were added and 3.38 W/L were applied. Obviously, the organic oxidation by-products formed are more recalcitrant to oxidation and require longer treatment times for their effective elimination. It is noted that even with a rather low irradiation dose (3.38 W/L) high system efficiencies (90–97%) can be achieved.

### 3.3 Combination of AO and H<sub>2</sub>O<sub>2</sub>/UV-C

Four experiments were carried out to examine whether system efficiency can be further optimized in comparison to the application of the AO and H<sub>2</sub>O<sub>2</sub>/UV-C methods, individually. Results are depicted in Fig. 4. The presence of 25 mM of electrolyte has a rather negative effect on TOC and color percentage removal; i.e., a decrease from 59% to 52% TOC and from 94% to 85% color respectively, after 6h of operation, despite the high value of current density obtained. Additionally, ‘on-line’ dosing of approx. 16 g/L H<sub>2</sub>O<sub>2</sub> after 12h of treatment led to better results (75% TOC and 90% color removal) compared to an experiment with ‘on-line’ dosing of approx. 13 g/L H<sub>2</sub>O<sub>2</sub> after 6h of treatment (42% TOC and 8% color removal) under the same current density (77 mA/cm<sup>2</sup>) and irradiation dose (5.9 W/L). The latter can be attributed to the much higher H<sub>2</sub>O<sub>2</sub> consumption; i.e., 77% instead of 34% (data not shown here).



**Figure 4.** Performance of combined electrochemical and photochemical oxidation after treatment with ‘on-line dosing’ of H<sub>2</sub>O<sub>2</sub>. Experimental conditions: pH 5.5–6.1, 800 mL/min, 5.9 W/L ■ 1064 mg/L TOCo, 1900 μS/cm, 25 mM Na<sub>2</sub>SO<sub>4</sub>, 77 mA/cm<sup>2</sup>, 6h ■ 800 mg/L TOCo, 6000 μS/cm, 300 mA/cm<sup>2</sup>, 6h ■ 1794 mg/L TOCo, 1772 μS/cm, 77 mA/cm<sup>2</sup>, 6h ■ 1819 mg/L TOCo, 1794 μS/cm, 77 mA/cm<sup>2</sup>, 12h

## 4. Conclusions

The performance of two advanced oxidation processes, i.e., AO and H<sub>2</sub>O<sub>2</sub>/UV-C and of their combination, is investigated for the treatment of wastewater originating

from the pesticide manufacturing industry. Main conclusions of this work are summarized as follows. Concerning AO, the increase of the wastewater flow rate reduces the ohmic resistance within the electrochemical cell leading to a higher current density. Almost total wastewater mineralization can then be achieved in shorter electrolysis times. The phosphorus-species transformation kinetics from organic to inorganic follow proportionally the kinetics of carbon removal. In case of high wastewater flow rates, the system efficiency was not favored by the aeration to the GDE cathode. The H<sub>2</sub>O<sub>2</sub>/UV-C process led to high system efficiencies and complete discoloration of the wastewater. Radiant power per unit volume as well as treatment time had significant positive effect on TOC percentage removal. The integration of the two technologies, appeared to be a very promising option; however, further investigation is needed. Although high system performance was achieved after 12h of operation with ‘on-line’ dosing of approx. 16 g/L H<sub>2</sub>O<sub>2</sub>, greater dosages of H<sub>2</sub>O<sub>2</sub> or longer treatment times are necessary, due to the refractory nature of the pollutants in this wastewater. Finally, the overall performance of the system is not affected by the presence of electrolyte and probably the AO acts rather synergistically with the main H<sub>2</sub>O<sub>2</sub>/UV-C process. In conclusion, the very encouraging results obtained in this study pave the way for further development of the investigated *hybrid AO/H<sub>2</sub>O<sub>2</sub>/UV-C process* for practical applications.

## 5. Acknowledgements

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## References

- Brillas, E., Sirés, I., Oturan, M.A. (2009), Electro-Fenton process and related electrochemical technologies based on Fenton’s reaction chemistry, *Chemical Reviews*, **109**, 6570–6631.
- Brillas, E., Martínez-Huitle, C.A. (2015), Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, *Applied Catalysis B: Environmental*, **166–167**, 603–643.
- He, Y., Lin, H., Guo, Z., Zhang, W., Li, H., Huang, W. (2019), Recent developments and advances in boron-doped diamond electrodes for electrochemical oxidation of organic pollutants, *Separation and Purification Technology*, **212**, 802–821.
- Oturan, M.A., Aaron, J.-J. (2014), Advanced oxidation processes in water/wastewater treatment: principles and applications, A Review, *Critical Reviews in Environmental Science & Technology*, **44**, 2577–2641.
- Panizza, M., Cerisola, G. (2005), Application of diamond electrodes to electrochemical processes, *Electrochimica Acta*, **51**, 191–199.